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Dipole strengths of chlorophyll-*a* and bacteriochlorophyll-*a*

RS Knox

University of Rochester, Rochester, NY USA 14627-0171 rsk@pas.rochester.edu

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Abstract. The dipole strength (D) of a chromophore in a given environment of refractive index n can be related to its intrinsic dipole strength in vacuum (D_{vac}) by $D(n) = f^2 D_{\text{vac}}$, where f is an index-dependent factor frequently taken to be that of Lorentz. The chlorophylls, as well as many simple chromophores, do not follow this rule very well. More success has been achieved with an “empty-cavity” factor. We present a simplified procedure for exporting and importing strengths among different environments. These considerations may help resolve some wide discrepancies in predicted Förster excitation transfer rates involving chlorophyll-*a*.

Introduction

The importance of dipole strength D to photochemistry and photobiology is not confined to extinction coefficients and lifetimes because strong interactions between chromophoric excitations contain these strengths as factors. Both exciton splittings and Förster rates of transfer depend on them (van Amerongen *et al.*, 2000).

Dipole strength is defined as the square of the electronic transition dipole moment of a band of transitions that are due to vibrational broadening of the electronic transition. Typical values of D for the first red peak in the chlorophylls are 20 to 60 debye², where 1 debye = 10^{-18} esu - cm (Shipman 1977, Connolly *et al.* 1982a,b; Alden *et al.* 1997). Observed dipole strengths depend on environment as well as the chromophore’s intrinsic properties. In the classical view, which we adopt here, the polarization of the environment by the chromophore itself augments the average field at the site of the chromophore, producing a different transition moment larger than the vacuum value.

Increasing availability of orientations and intermolecular distances, through protein structure determinations, has sparked interest in more precise estimates of excitation transfer rates. The Förster (1948) theory assumes that transition strengths are known *as measured in the transferring medium*, whereas in nearly all cases one must infer strengths from measurements outside that medium. It is common practice to use effective field factors to correct for this difference. We suggest here a simplified way of estimating the effect of the environment on D , with specific application to the chlorophyll-*a*’s.

Methods

Our analysis is based entirely on literature data. Central papers are those of Seely and Jensen (1965), Shipman (1977), Connolly *et al.* (1982a, 1982b), and Alden *et al.* (1997). The dipole strength D associated with an extinction coefficient $\epsilon(\tilde{\nu})$, where $\tilde{\nu}$ is photon energy, is (Förster 1948; Moog *et al.* 1984)

$$D = \mu^2 = 9.186 \times 10^{-3} n \int [\epsilon(\tilde{\nu}) / \tilde{\nu}] d\tilde{\nu} \quad (1)$$

in debye². $\epsilon(\tilde{\nu})$ is in liters/(mol cm), μ is the transition matrix element of the spectral feature under consideration, and n is the refractive index of the medium in which $\epsilon(\tilde{\nu})$ is measured. The numerical factor is $(3 \times 10^{39} hc \ln 10) / (8\pi^3 N_A)$, where h is Planck's constant, c the speed of light, and N_A Avogadro's number.

Extracting the strength of the lowest-energy peak of from a broadened vibronic spectrum brings with it a systematic error due to approximating the remainder of the band.

Recognizing the inevitable few-percent uncertainty in this case, we evaluate the integral of Eq. (1) by replacing the denominator of the integrand with the energy at the maximum of the peak $\tilde{\nu}_{\max}$ and using the half-Gaussian method introduced by early workers (*e. g.*, Seely and Jensen 1965). The line is assumed Gaussian and its half-width δ (taken in the same units as $\tilde{\nu}_{\max}$) is determined by assuming that the higher bands are negligible at the peak and to longer wavelengths. The area is then determined from δ and the extinction coefficient ϵ_{\max} of that peak by

$$\int \epsilon(\tilde{\nu}) d\tilde{\nu} / \tilde{\nu} \sim 2.13 \epsilon_{\max} \delta / \tilde{\nu}_{\max} . \quad (2)$$

Here the numerical coefficient is $\sqrt{(\pi/\ln 2)}$. We restrict our analysis to this “0–0” transition, since it contributes most heavily to most Förster processes, and the full strength is proportional to its strength. In chlorophyll-*a*, this avoids an additional extraction problem because the full Q_y transition is overlapped by the Q_x transition.

If the chromophores under consideration were situated in vacuum, Eq. (1) with $n = 1$ and $\epsilon(\tilde{\nu}) = \epsilon_{\text{vac}}(\tilde{\nu})$ would provide a quantity $D_{\text{vac}} = \mu_{\text{vac}}^2$, a quantity reproducible in principle from a quantum chemical description of ground- and excited-state wave functions. As a practical matter, the effect of the medium has generally been handled by an index-dependent correction such as the Lorentz factor f_L^2 :

$$D = f_L^2 D_{\text{vac}}, \quad \text{where } f_L^2 = [(n^2 + 2) / 3]^2 . \quad (3)$$

Long ago Chako (1934) found very little success in applying Eq. (4) to a wide variety of organic chromophores and solvents. A competing model is that of a “true cavity” wherein the chromophore is assumed to be at the center of a spherical cavity whose inner surface attains induced charges due to the incident field. In this case (Böttcher 1973)

$$D = f_C^2 D_{\text{vac}}, \quad \text{where } f_C^2 = [3n^2 / (2n^2 + 1)]^2 . \quad (4)$$

The index-dependent factors are discussed by van Amerongen *et al.* (2000), pp. 58–59.

Results and discussion

To evaluate the relative merits of Eqs. (3) and (4), Alden *et al.* (1997) plotted bacteriochlorophyll-*a* dipole strengths as a function of solvent index. We have adopted this idea for the Q_y transition of chlorophyll-*a* (Fig. 1). Most points are taken from Seely and Jensen (1965). The two points marked by heavy triangles have been added after minor corrections and were taken from Houssier and Sauer (1970) and Sauer *et al.* (1966). In the former case the solvent was ethyl ether, $n = 1.35$, and in the latter it was CCl_4 , $n = 1.46$. The 0–0 band values reported in these papers were 21.7 and 24.7 debye², respectively, but these were determined from an equation that did not contain the factor n of Eq. (1). For ether, the new result is 29.3 debye². The CCl_4 strength was adjusted in the same way and then recomputed by our standard method for the 0–0 peak, with the result 31.1 debye². For the points just described, a linear best fit may be proposed for this dipole strength:

$$D = 20.07 + 24.31(n-1) \text{ debye}^2 \quad (Q_y \text{ "0-0", Chla}) \quad (5)$$

For this fit the correlation coefficient is 0.70 and all points shown in the figure are included. Pending further analysis we exclude the more recent chlorophyll-*a* data of Lichtenthaler (1987) because the implied strengths, measured in ethyl ether and aqueous ethanol, are 25% higher than the corresponding points in Fig. 1. An independent treatment of the Seely-Jensen ether data by Shipman and Hausman (1979) confirms our corrected value of 29.3, despite the fact that the principal contributions to the 0–0 line literally add up to only 16.7 debye². In their analysis the integral over the spectrum is divided instead of multiplied by n . The corrected result is 30.4 debye², close to our linear fit and to our own recalculation of 28.2 debye².

Dipole strengths are also factors in chromophore radiative rates. Monshouwer *et al.* (1997) used measured bacteriochlorophyll-*a* rates to deduce its Q_y dipole strength. Connolly *et al.* (1982a) measured fluorescence rates of chlorophyll-*a* in various solvents.

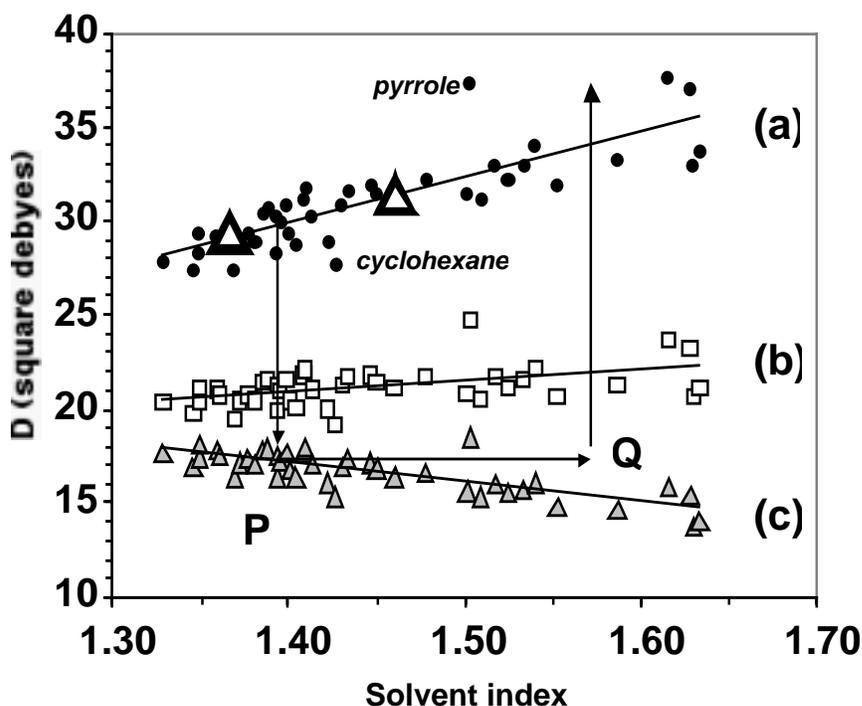


Figure 1. Dipole strength as a function of solvent index. (a) Experimental points (see text) and least-squares linear fit. (b) Vacuum-value linear fit using cavity factor. (c) Vacuum value linear fit using Lorentz factor. Arrows, P, and Q illustrate the current method of estimating the effect of an index change (see text).

We have used them in a rather broad test of our assignment of dipole strengths and the accuracy of Eq. (5). They range from 0.26 to 0.38, clearly of the right order of magnitude.

We have repeated this study for bacteriochlorophyll-*a*, largely using absorption data by Connolly *et al.* (1982b). The empirical fit to measured dipole strengths for this lot is

$$D = 46.07 + 26.20 (n - 1) \text{ debye}^2 \quad (\text{Q}_y, \text{“0-0”}, \text{Bchl-}a). \quad (6)$$

We now argue that the vacuum dipole strength is *unnecessarily* troublesome in discussions of excitation transfer and exciton interactions, unless there is an explicit need for a theoretical value. If an index-related unique value *were* obtainable, the vacuum line corresponding to those in Fig. 1 would be perfectly horizontal. Here, this does not occur with either cavity model. Rather than rely on vacuum strengths, one can simply use the empirical relationship between *D* and the index. When a cavity or Lorentz factor is used, it is based on the assumption that the medium can be characterized by a single parameter *n*; *nothing is added* by going through the exercise of twice applying a factor f_L^2 or f_C^2 .

Consider the scenario that accompanies the arrows in Fig. 1. A chromophore with strength 30 in a medium of index 1.38 is to be placed in a medium of index 1.57, and its new strength estimated. The current method is first to find a vacuum value (arriving at point P, 17 debye²). This value is tacitly assumed to be a constant and the Lorentz factor is reapplied (starting at Q). The result is 37, so obviously an error has been made. Let us now suppose that a vacuum line really is horizontal. Going through P and Q returns us directly to the empirical line; therefore the procedure might well not have been performed at all.

The empirical relations (5) and (6) are crude but produce reliable values to within the obvious visible error of the scatter of the data. More precision may be possible if separate curves are set up for groups of chemically similar solvents. The corrections and procedural improvements described here are capable of narrowing the range of predicted Förster rates involving Chl-*a* and Bchl-*a*. These results will be presented elsewhere.

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